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COMPLETE SPECIFICATION

High Temperature Stainless Steel

We, ALLOY RESEARCH CORPORATION, a corporation organized and existing under the laws of the State of Delaware, United States of America, located at 3400, East Chase Street, Baltimore, 13, State of Maryland, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

The present invention relates to high temperature stainless steel and products and articles made of the steel.

The steel of this invention is strong and durable, it has good hot working properties and its products and articles have highly satisfactory resistance to stress rupture and creep while hot and under load, are well suited for resisting attack by hot corrosive matter and the formation of heat scale. The high temperature properties are enhanced by appropriate heat treatment.

Austenitic chromium-nickel stainless steels of the ordinary grades containing 10% to 25% chromium and 7% to 15% nickel have heretofore been widely used in the form of low temperature or mildly heat resistant products or articles of manufacture. By virtue of the presence of nickel, these stainless steels have a relatively high alloy content as compared with straight chromium ferritic stainless steels and are better suited to resist oxidation than are these steels when heated to high temperatures say for example about 1000° F.

There is still the existing fact, however, that austenitic stainless steels of the character just noted are unsatisfactory for meeting exacting demands at high temperatures where used for example as bolts and fasteners, internal combustion engine valves, gas and steam turbine blades, rotors, buckets, nozzles, supercharger components, or as any of a host of other products and articles subjected to load while extremely hot. Such products, when made of these steels are too susceptible to creep and stress-rupture under the severe heat.

The conventional austenitic chromium-nickel stainless steels referred to, accordingly, have gained popular demand in the form of such low temperature products as trim for house, store, office or restaurant purposes, or vehicle trim and other products capable of resisting the effects of weather. These steels too are very much in demand as cooking utensils, tableware, receptacles and other appliances where a metal of enduring brightness is needed to withstand body salts, fruit acids and other corrosive compounds. Among the better known products of this class are those made of the usual 18% chromium—8% nickel steels which are readily worked as by rolling, drawing, spinning, and the like, to desired form.

While the austenitic stainless steels of the character noted give better all-round service at low temperatures, they still have a more favorable lattice structure for cohesion under stress or load at elevated temperatures than do ferritic straight-chromium stainless steels. This comparison, however, does not necessarily assure adequate high-temperature properties, especially with respect to such considerations as resistance to stress-rupture and creep.

It has now been found that by correlating proper amounts of the ingredients chromium, nickel, cobalt, manganese, molybdenum, copper, carbon, titanium and niobium to provide an austenitic stainless steel, satisfactory hot-working properties are had along with excellent high temperature strength and resistance to heat and corrosion. The steel forming the object of the invention contains 12% to 22% chromium, 0.5% to 10% nickel, from 4% to 40% cobalt, manganese up

to 2%, 1% to 4% molybdenum, from 2% to 4% copper, carbon up to 0.35%, from 0.15% to 0.75% titanium, 0.20% to 1.10% niobium, and the remainder iron plus impurities. Such elements as sulphur and phosphorus preferably are less than 0.04% each.

We often form the steel by such steps as hot working and machining, into any of a host of high temperature products and articles, among which are bolts, fasteners, rivets, chemical equipment parts, tubes, such as seamless tubes formed by piercing and drawing, gas and steam turbine blades, rotors, buckets, nozzles and supercharger parts for serving under mechanical stress or resisting corrosion during their intended use. The high temperature products and articles of manufacture are strong, durable and reliable. They resist creep and stress-rupture while hot.

There are occasions where we provide products of the steel in such form as sheet, strip, wire, rods, or the like which are readily useful for fabrication as by cutting, punching, bending, or welding as by means of oxy-acetylene or arc welding equipment, into desired shape. Sometimes, too, we use the sheet, wire, or the like, directly in high temperature applications without appreciable further fabrication.

The steel and articles and products made from the same are wholly austenitic. Ferrite, if present at all, is only in traces. This we find is essential to the required stress-rupture properties. Where appreciable amounts of ferrite are present the stress-rupture values fall off; also, the working properties suffer. The substantial quantity of cobalt which we employ not only supplements the effect of nickel to assure an austenitic balance, but improves the stress-rupture properties and serves to cut down development of sigma phase. Also, with the cobalt constituent, a steel of relatively high alloy content is had in favour of better scaling resistance under intense heat.

With any appreciable lowering of the copper and molybdenum contents to outside the ranges hereinbefore noted, the high temperature load carrying capacity of the steels suffer, and with appreciable increase beyond the ranges, workability disappears. The elements titanium and niobium in the amounts indicated enhance the stress-rupture and creep properties, and give improvements in the high temperature load-carrying ability, particularly after proper heat treatment of the steel.

In heat treating the steel for enhancing the high temperature properties, we include operations in the form of annealing and precipitation treatment. To effect this combined treatment, we heat up the steel, as for example, roughly shaped articles thereof, first to temperatures where titanium and niobium go into solution. These temperatures preferably range from 2050° F. to 2250° F. The titanium is quite soluble throughout this heating range and the niobium becomes more soluble toward the upper end of the range. Copper also goes into solution. Working operations are achieved on the metal, if desired, either before, along with, or following the annealing treatment.

Upon treating the steel at solution temperature for a sufficient period of time, we thereafter quench the steel as in air, oil or water, conveniently to about room temperature. Subsequently, we heat the quenched steel up to a temperature preferably within the range of 1200° F. to 1500° F. where a critically dispersed, finely divided precipitate comes out in the metal lattice along the slip planes in the matrix. In this, there is a precipitation of intermetallic compounds including titanium and niobium. Copper comes out in fine form, or possibly as an intermetallic compound comprising such elements as nickel, titanium and niobium. Some portion of the precipitated elements, such as the titanium and niobium is in the form of carbides which increase in amount toward the high side of the precipitation temperature range just noted.

At the completion of the precipitation heat treatment, we quench the steel. The quenched metal has a fine grain structure, and is further characterized by enhanced load-carrying capacity in view of atomic slip-interference developed by the precipitates. The steel in this condition often is worked, fabricated or finished to give articles or products. During high temperature use of the steel, the precipitates remain critically dispersed, uncoalesced and effective against creep and stress-rupture for long periods of time. Any heating of the steel to so high as the solution temperature of course tends to put the precipitate back into solution.

A few examples of the austenitic chromium-nickel-cobalt stainless steels which we provide are identified in Table I. These steels in addition to containing (in per cent.) the amounts of ingredients noted, have a remainder which is iron plus impurities.

TABLE I.

CHROMIUM-NICKEL-COBALT STAINLESS STEELS.

Steel	C	Mn	P	S	Si	Cr	Ni	Mo	Cu	Nb	Ti	Co
A	.087	.65	.018	.011	.43	15.50	8.93	2.00	3.10	.26	.16	14.90
B	.131	.67	.017	.008	.59	15.35	8.15	2.40	3.05	.40	.27	13.60
C	.086	.71	.018	.009	.51	17.17	9.01	2.05	2.95	.36	.18	19.80
D	.130	.62	.018	.011	.50	15.77	6.09	1.60	2.95	.40	.25	15.00
E	.133	.63	.014	.008	.65	15.80	9.01	2.38	3.05	.44	.27	10.00
F	.167	.76	.017	.010	.62	20.51	9.02	1.72	3.05	.58	.31	34.80
G	.135	.61	.018	.016	.45	16.37	5.01	1.91	3.04	.44	.25	10.07
H	.203	.59	.017	—	.60	19.47	5.12	2.09	2.85	.47	.30	39.90
I	.143	.59	0.17	—	.53	16.18	5.12	2.04	2.87	.53	.28	29.50
J	.134	.63	.019	.018	.43	16.27	3.03	1.93	2.99	.47	.24	15.42

All of the steels in Table I were subjected to a solution heat-treatment at 2250° F. for one-half hour followed by quenching in water plus precipitation heat-treatment at 1350° F. for five hours and quenching in air. After the annealing and precipitation treatments, samples of these steels were given stress-rupture tests with the results noted in Table II.

TABLE II.

STRESS-RUPTURE TESTS OF CHROMIUM-NICKEL-COBALT STAINLESS STEELS.

Steel	Load (psi) Endured at 1200° F. for:		Load (psi) Endured at 1500° F. for:	
	100 hrs.	100 hrs.	100 hrs.	1000 hrs.
A	47,000	43,000	17,000	11,600
B	53,000	47,000	18,000	13,700
C	50,000	43,000	18,000	11,500
D	47,000	41,000	18,000	14,000
E	47,000	43,000	17,000	14,000
F	52,000	47,000	20,000	15,000
G	—	—	17,200	13,200
H	—	—	20,500	14,600
I	—	—	19,800	14,200
J	—	—	18,000	12,000

These austenitic chromium-nickel-cobalt stainless steels have many valuable properties, including resistance to stress-rupture and resistance to creep whether or not the steels and products and articles thereof are in the precipitation heat treated condition. The precipitation heat treatment enhances a number of the properties by the development of atomic slip-interference. Also, the steels, despite the high temperature properties of the same are capable of fabrication with relative ease as compared with many high temperature steels of the ferritic grade.

Thus it will be seen that there are provided in this invention austenitic chromium-nickel-cobalt alloy stainless steel and products thereof in which the various objects noted together with many thoroughly satisfactory results are successfully achieved. It will be seen that the products are tough, strong and durable, corrosion-resistant and heat-resistant and serve well at high temperatures over long periods of time under many conditions of actual practical use.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. Austenitic chromium-nickel-cobalt stainless steel, containing 12% to 22% chromium, 0.5% to 10% nickel, from 4% to 40% cobalt, up to 2% manganese, 1% to 4% molybdenum, 2% to 4% copper, from 0.15% to 0.75% titanium, 0.20% to 1.10% niobium, up to 0.35% carbon, and the remainder iron plus impurities.

2. Stainless steel as claimed in claim 1 containing each of the elements sulphur and phosphorus in an amount not exceeding 0.04%.

3. Wrought stainless steel articles having the composition claimed in claim 1 or 2.

4. Method of producing austenitic stainless steel and steel articles composed as claimed in claim 1 or 2 characterized by heating the steel or the steel articles at such temperature as to provide at least a portion of its copper, titanium and niobium in solid solution preferably 2040° F. to 2250° F. then quenching the same and re-heating at temperatures sufficiently high and for long enough time to achieve precipitation and critical dispersion of a finely divided precipitate including copper, titanium and niobium from solution, preferably 1200° F. to 1500° F., thus increasing high temperature load carrying capacity of the stainless alloy metal.

5. Austenitic stainless steel whenever produced in accordance with claim 4.

6. Austenitic stainless steel articles whenever produced in accordance with claim 4.

7. Austenitic chromium-nickel-cobalt stainless steel and articles made of this steel as described.

Dated this 23rd day of August, 1949.

MARKS & CLERK.

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